One-Time Password Generation and Two-Factor Authentication Using Molecules and Light

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A Basic Step toward One-Time Password Generation and Two-Factor Authentication Using Molecules and Light

Gaowa Naren,[a] Shiming Li,[a] and Joakim Andréasson*[a]

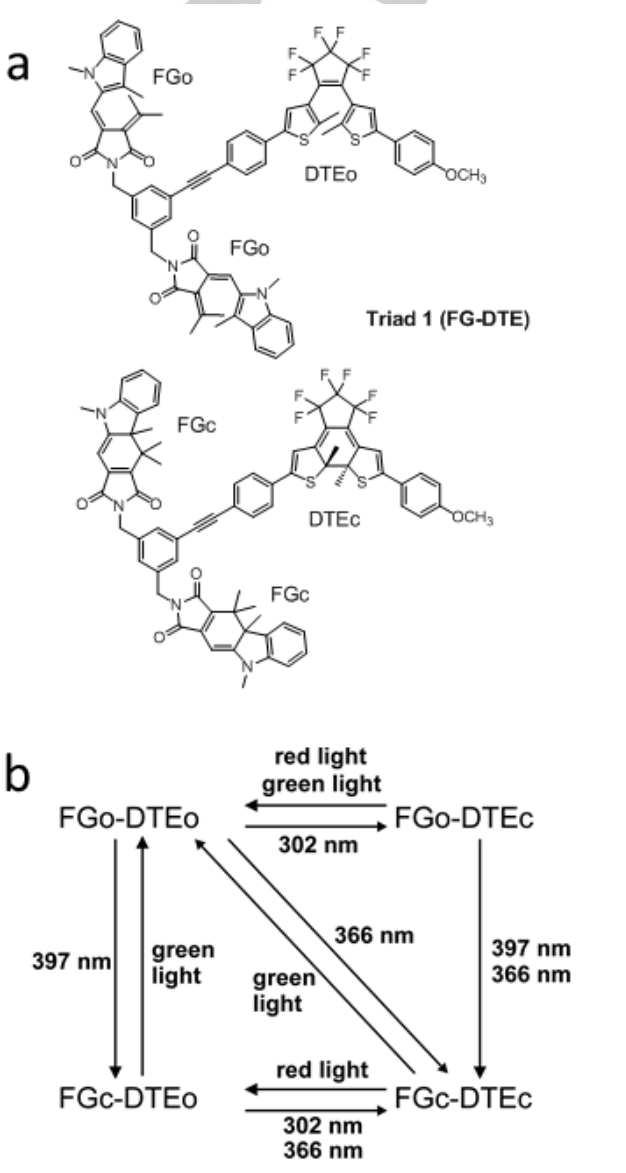
Abstract: Herein, we report the first example of One-Time Password (OTP) generation and Two-Factor Authentication (TFA) using a molecular approach. OTP:s are passwords that are valid for one entry only. The next login session, a new, different password is generated. This brings the advantage that any undesired recording of a password will not risk the security of the authentication process. Our molecular realization of the OTP generator is based on a photochromic molecular triad where the optical input required to set the triad to the fluorescent form differs depending on the initial isomeric state.

The collective research effort on molecular logic has resulted in the mimicry of many of the operations performed by silicon based processors.[1-4] What started off as a "one molecule:one logic gate"[5-9] relation has now developed into a field where one molecule can mimic the function of up to 16 logic devices,[10] including addition/subtraction,[11-16] multiplexing/demultiplexing,[17-21] encoding/decoding,[22-24] parity generation/checking,[25] latches/flip-flops,[26-27] and sequential[28-31] as well as reversible[32-33] logic. In terms of security- and authentication devices, the molecular keypad lock has enjoyed clear preference.[29] The keypad lock is a sequential logic device (in principle a priority AND-gate) where the output is sensitive not only to the correct input combination, but also to the order by which the inputs were applied. For example, entering the PIN code to an ATM machine requires the application of four digits chosen from 0 to 9 in the correct order, and not in any of the other 23 possible permutations of these digits. The majority of the molecular keypad locks, however, are using two inputs only, dramatically reducing the number of possible permutations to two.

In order to further strengthen the security in authentication processes (such as the entry of a PIN-code), One-Time Passwords (OTP) can be used, often in combination with two-factor authentication (TFA). OTP:s are "non-static" passwords, i.e., they are valid for one entry only. This increases the security dramatically, as a password stolen by intrusion will not give the intruder access to the protected system.

The two factors in TFA are often referred to as something the user *has* and something that the user *knows*. An illustrative example of this is your bank card in combination with the PIN-code. Access to money withdrawal from your bank account is not granted unless you *have* the card and *know* the PIN-code.

Here, we report the first, basic, molecular implementation of OTP generation in combination with TFA. Our approach relies on the fluorescent and photochromic properties of Triad **1**[22] shown in Scheme 1.



Scheme 1. Structure and isomerization scheme of Triad **1**. (a) The Triad shown with the photoswitches in the open forms (FGo-DTEo, upper structure) and in the closed form (FGc-DTEc, lower structure). FGo-DTEo displays absorption only in the UV region, whereas FGc-DTEc displays absorption also in the visible. For structures of the model monomers referred to in the text, see Figure S1 in the Supporting Information. (b) Isomerization pathways between the different forms of Triad **1**.

The photophysical properties of the triad has been described in detail.[22] Briefly, it consists of two identical photoswitches from the fulgimide (FG) family together with a

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Supporting information for this article is given via a link at the end of the document.

single dithienylethene (DTE) photoswitch. Both FG and DTE exist as two (constitutional) isomers: the open and the closed forms. These are referred to as FGo, DTEo, FGc, and DTEc, respectively. Hence, there are in total four states of Triad **1**, assuming identical isomeric forms of the two FG units: FGo-DTEo, FGc-DTEo, FGo-DTEc, and FGc-DTEc. The open forms FGo and DTEo absorb almost exclusively in the UV region and isomerize to the closed versions FGc and DTEc by exposure to UV light. The reverse ring-opening reactions are triggered by the exposure to visible light (see Scheme 1). Due to the spectrally distinct absorption bands (see Figure 1) and the ratio between the isomerization yields of the ring closing reactions (see Table 1), FGo and DTEo can be isomerized with very high selectivity to the respective closed isomer in Triad **1**.

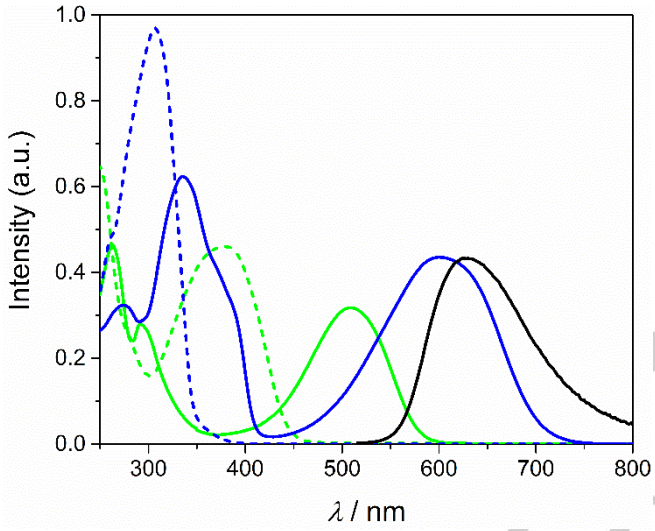

Figure 1. Absorption and emission spectra of the FG and DTE model monomers in 2-methyltetrahydrofuran. The absorption of FGo (green dotted line), DTEo (blue dotted line), FGc (green solid line), DTEc (blue solid line), are shown together with the fluorescence spectrum of FGc upon excitation at 500 nm (black solid line). The absorption spectra have been scaled to represent the 2:1 relation between FG and DTE in Triad **1**. For the structures of the model monomers, see Figure S1 in the Supporting Information.

As shown in Scheme 1, DTEo is preferably isomerized to DTEc by the use of 302 nm light, whereas the optimal wavelength for FGo is 397 nm. 366 nm is used to isomerize both photoswitches to the closed forms. As for the reverse reactions, the FGc-DTEc form is isomerized to FGo-DTEo by green light exposure, whereas red light leads to the formation of FGc-DTEo (see Figure S2 in the Supporting Information for spectra of Triad **1** highly enriched in all four isomeric forms). The isomerization properties of FG and DTE are collected in Table 1.

FGc emits moderately strong emission ($\Phi_F \approx 0.01$) centered at around 630 nm. From Figure 1, it is seen that there is a significant overlap between the emission of FGc and the absorption of DTEc. Thus, FRET quenches the emission of FGc in the FGc-DTEc isomeric form with virtually unity efficiency (from τ_F = 135 ps in the reference monomer to τ_F < 5 ps in the FGc-DTEc form of Triad **1**,[22] implying that the only state of the triad that displays fluorescence emission upon excitation at 500 nm is FGc-DTEo. As described below, these observations are used to realize the TFA and the OTP generation of Triad **1**.

Table 1. Quantum yields for the photoinduced isomerization reactions of the model monomers

Compound[a]	Photoisomerization	Φ_{iso} [b]
FG model	FGo → FGc	0.10
FG model	FGc → FGo	0.20
DTE model	DTEo → DTEc	0.34
DTE model	DTEc → DTEo	0.0077

[a] See structures in Figure S1 in the Supporting Information. [b] Isomerization quantum yields.

In our interpretation of the operation, the first step is to use Triad **1** as a 2-input priority AND gate (PAND gate), equivalent to a 2-input keypad lock.[10] This is conveniently done by setting the triad to the FGo-DTEo initial state by exposure to green light (460 nm < λ < 590 nm, 30 min exposure time). The two inputs are then defined as In1 = 366 nm UV light (45 s exposure time) and In2 = red light (λ centered at 623 nm, 2.5 min exposure time). The output used is fluorescence emission from FGc at 624 nm (Out) after excitation at 500 nm. In the context of TFA, what the user must *know* here is how to convert the triad from the non-fluorescent isomer FGo-DTEo to the fluorescent isomer FGc-DTEo. This directly translates into knowing which one of the eight possible ordered input combinations of In1 and In2 that switches the output to the *on*-state, giving the user access to the system. From Scheme 1, it is clear that In1 (366 nm UV) followed by In2 (red light) results in the population of FGc-DTEo, whereas all other input combinations result in the formation of non-fluorescent isomeric forms. The emission intensities after all eight input combinations are shown in Figure 2.

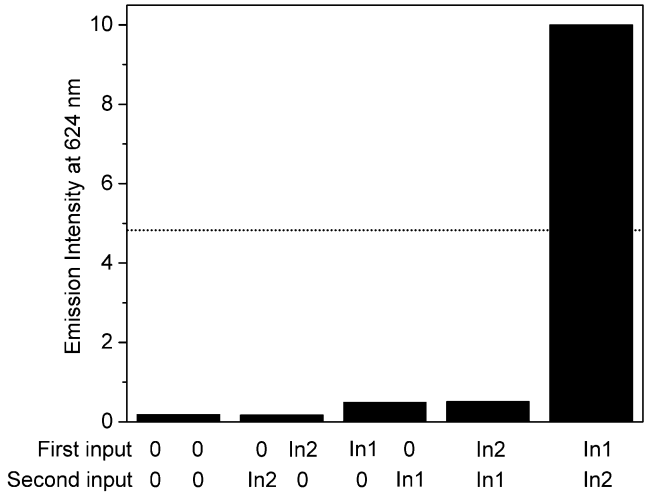

Figure 2. Triad **1** as a 2-input PAND gate (keypad lock). In1=366 nm UV, In2=red light (λ centered at 623 nm). The fluorescence intensity used as the output exceeds the threshold level (dotted line, distinguishing an *on* output from

an *off* output) only after one of the eight possible ordered input combinations. Excitation wavelength for emission readout = 500nm.

Next, Triad **1** is again reset (by the security system) to the initial state FGo-DTEo by exposure to green light. Subsequent to this operation, the security system either exposes the triad to 366 nm UV light, converting the triad to the non-fluorescent FGc-DTEc form, or, alternatively, leaves it unexposed in the non-fluorescent FGo-DTEo form. This choice is done randomly by the system itself. We refer to this step as the "set" operation. Thus, in this step, the system selects randomly "set = 0" or "set = 366 nm". Although both these isomeric states are non-fluorescent, they can be distinguished by their absorption spectra (see Figure S2 in the Supporting Information). The FGo-DTEo isomer displays strong absorption at 330 nm, but weak absorption at 640 nm. FGc-DTEc, on the contrary, absorbs strongly at 640 nm, but only weakly at 330 nm. These features are easily read by the system by photonic means, and can be communicated to the user by the notions "high" or "low" at two wavelengths.

In the final step of the process, the user has to enter the correct "password" to be fully authenticated. As the output is again defined as fluorescence emission, this is successfully done only if Triad **1** is isomerized to the FGc-DTEo isomer. Depending on if the triad was left in the FGo-DTEo form ("set = 0") or isomerized to the FGc-DTEc form by 366 nm UV exposure ("set = 366 nm") in the randomized "set" operation by the system, the triad should be exposed to 397 nm light (In = 397 nm, 3 minutes exposure time) or red light (In = red, 2.5 min exposure time), respectively. Figure 3 shows the actual fluorescence intensities resulting from the different "set" and "password" combinations. This boils down to the situation described by the "key" shown in Table 1:

Table 1. The "key" for OTP required in the TFA process.

Isomeric form after the "set" operation	Abs. @ 330 nm	Abs. @ 640 nm	Input (password) required for authentication
FGo-DTEo	High	Low	In = 397 nm
FGc-DTEc	Low	High	In = red

Here, it is obvious that the correct password is different in the two cases, and it depends again on the randomized "set" operation. Without the "key", however, the absorption data at 330 nm and 640 nm given to the user by the system is useless. In terms of TFA, this "key" is what the user must *have*. As the user also must *know* the correct input combination of In1 and In2 to get access to the system in the first step (2-input PAND gate, Figure 2), the requirements for TFA are fulfilled.

To summarize, we have described the first example of a molecule capable of One-Time Password (OTP) generation and Two-Factor Authentication (TFA). Different combinations of optical inputs (used for isomerization purposes) are needed to convert the photochromic Triad **1** to the fluorescent form, depending on the initial state. These combinations are defined as the passwords (inputs) required to authenticate the user by emission of fluorescence (output). The all-photonic nature[34] of the function allows for repeated operation[22] without buildup of chemical waste. It also implies that the system can be totally

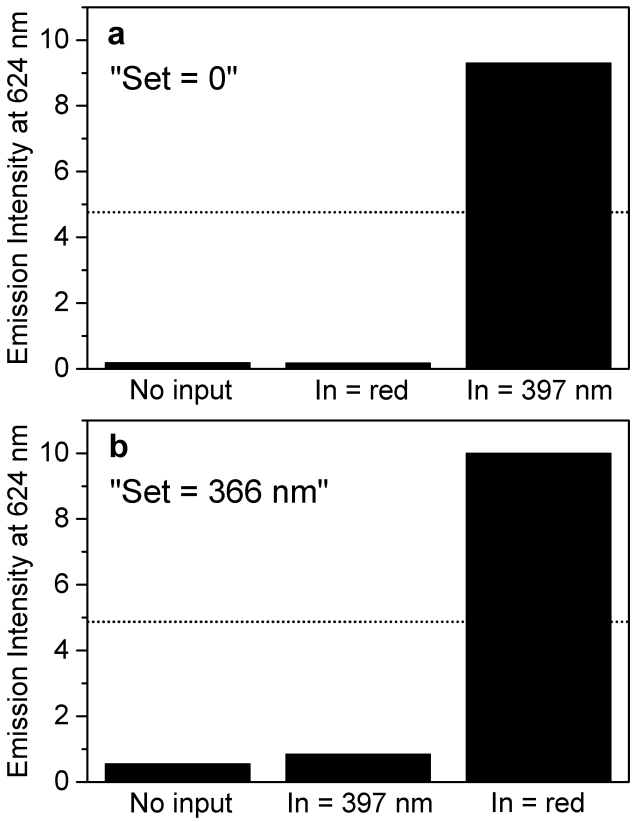

Figure 3. Emission intensities at 624 nm (output) after exposure to In = 397 nm light or In = red light subsequent to the two different "set" operations. Excitation wavelength for emission readout = 500nm. The dotted lines represent the threshold levels, distinguishing an *on* output from an *off* output.

"closed", as physical access to the system for, e.g., the addition of chemicals, is not required. It is acknowledged that Triad **1** can only generate a total of two different passwords. In turn, this results in a very low complexity of the "key", which could in principle have been memorized for this specific case. This implies, of course, that the device reported in this study is too limited for any practical application. However, we hope that this report will spark the interest of other practitioners in the same research field to develop this concept further.

Experimental Section

2-methyltetrahydrofuran was the solvent for spectroscopic measurements. The absorption measurements were performed using a CARY 4000 UV/vis spectrometer. A SPEX Fluorolog-3 was used for the emission measurements. After exposure to the different input combinations, the absorbance and emission were monitored separately using the

instruments mentioned above. The sample concentration was ~ 2.5×10^{-5} M. The 397 nm light was supplied by the lamp and the monochromator of the abovementioned fluorometer. The broad band green light was generated by a 500 W Xe lamp equipped with a hot mirror (A=1.8 at 900 nm) to reduce the IR intensity and a VG 9 glass filter (A<1.5 between 460 nm and 590 nm). A LZ1-00R100 Red LED emitter (centered at around 623 nm) was used for the red light. The 366 nm UV light was generated by a UVP hand-held UV lamp (Model UVGL-25).

Acknowledgements

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Keywords: photochromism • photoswitches • molecular devices • molecular logic • fluorescence

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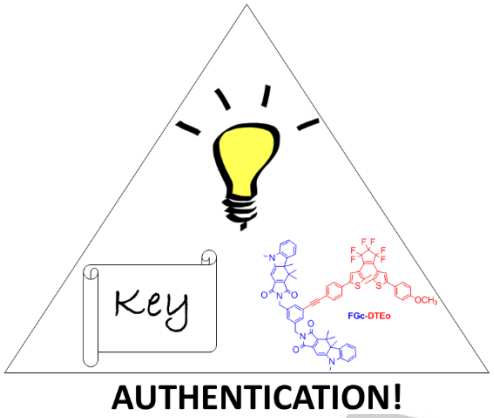
Entry for the Table of Contents

COMMUNICATION

A photochromic molecular triad is used to generate one-time passwords using two-factor authentication. The function relies on finding the right optical input combination, resulting in the formation of the fluorescent isomeric form of the triad.



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